



Technical Support Document for Best Management Practices for Spent Pulping Liquor Management, Spill Prevention and Control

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**TECHNICAL SUPPORT DOCUMENT
FOR
BEST MANAGEMENT PRACTICES FOR
SPENT PULPING LIQUOR MANAGEMENT, SPILL PREVENTION, AND CONTROL**

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SPECIALIZED DEFINITIONS

- (1) *Action Level:* A daily pollutant loading that when exceeded triggers investigative or corrective action. Mills determine action levels by a statistical analysis of six-months of daily measurements collected at the mill. For example, the lower action level may be the 75th percentile of the running seven-day averages (that value exceeded by 25 percent of the running seven-day averages) and the upper action level may be the 90th percentile of the running seven-day averages (that value exceeded by 10 percent of the running seven-day averages).
- (2) *Equipment Items in Spent Pulping Liquor, Soap, and Turpentine Service:* Any process vessel, storage tank, pumping system, evaporator, heat exchanger, recovery furnace or boiler, pipeline, valve, fitting, or other device that contains, processes, transports, or comes into contact with spent pulping liquor, soap, or turpentine. Sometimes referred to as “equipment items.”
- (3) *Immediate Process Area:* The location at the mill where pulping, screening, knotting, pulp washing, pulping liquor concentration, pulping liquor processing, and chemical recovery facilities are located, generally the battery limits of the aforementioned processes. “Immediate process area” includes spent pulping liquor storage and spill control tanks located at the mill, whether or not they are located in the immediate process area.
- (4) *Intentional Diversion:* The planned removal of spent pulping liquor, soap, or turpentine from equipment items in spent pulping liquor, soap, or turpentine service by the mill for any purpose including, but not limited to, maintenance, grade changes, or process shutdowns.
- (5) *Mill:* The owner or operator of a direct or indirect discharging pulp, paper, or paperboard manufacturing facility.
- (6) *Senior Technical Manager:* The person designated by the mill manager to review the BMP Plan. The senior technical manager shall be the chief engineer at the mill, the manager of pulping and chemical recovery operations, or other such responsible person designated by the mill manager who has knowledge of and responsibility for pulping and chemical recovery operations.
- (7) *Soap:* The product of reaction between the alkali in kraft pulping liquor and fatty acid portions of the wood, which precipitate out when water is evaporated from the spent pulping liquor.

- (8) *Spent Pulping Liquor*: For kraft and soda mills “*spent pulping liquor*” means black liquor that is used, generated, stored, or processed at any point in the pulping and chemical recovery processes. For sulfite mills “*spent pulping liquor*” means any intermediate, final, or used chemical solution that is used, generated, stored, or processed at any point in the sulfite pulping and chemical recovery processes (e.g., ammonium, calcium, magnesium, and sodium base sulfite liquors).
- (9) *Turpentine*: A mixture of terpenes, principally pinene, obtained by the steam distillation of pine gum recovered from the condensation of digester relief gases from the cooking of softwoods by the kraft pulping process. Sometimes referred to as *sulfate turpentine*.

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1.0 INTRODUCTION

This document presents information for Best Management Practices (BMPs) for bleached papergrade kraft and soda, and papergrade sulfite mills. EPA promulgated these BMPs pursuant to section 304(e), section 307(b) and (c), section 402(a), and section 501(a) of the Clean Water Act (CWA) for mills subject to 40 CFR Part 430, Subpart B - Bleached Papergrade Kraft and Soda, and Subpart E - Papergrade Sulfite.

The BMPs establish controls that will reduce the release of toxic, conventional, and non-conventional pollutants to navigable waters. The principal objective of the BMPs is to prevent losses and spills of spent pulping liquor (also referred to as "black liquor" at kraft mills) from equipment items in pulping liquor service; the secondary objective is to contain, collect, and recover, or otherwise control, spills, losses and intentional liquor diversions that do occur. The BMPs also apply to pulping by-products, such as turpentine and soap, for mills that process these items.

Economic operation of kraft and sulfite pulping processes is predicated on the recovery of inorganic pulping liquor chemicals and energy from the organic material dissolved from the wood supply during the pulping processes. However, the nature of pulp screening, washing and pulping liquor recovery systems is such that losses of spent pulping liquors (e.g., kraft black liquor and sulfite red liquor) are routine. Liquor is lost from seals on brownstock washers, pumps and valves in liquor service, knotters and screens, sewerage evaporator boil-out solutions, and other intentional liquor diversions during maintenance, startups and shutdowns. Spent pulping liquor is also lost in spills resulting from process upsets, tank overflows, mechanical breakdowns, operator errors, and construction activities. Research into spill incidents reported through EPA's Emergency Response Notification System shows that only a few pulping liquor

spills have resulted from catastrophic failures of bulk liquor storage tanks. Mechanical failure was cited in 45% of reported liquor spills, human error in 20%, tank overfilling in 16%, and intentional diversions in 4%. The cause of 13% of the spills was reported as unknown. In addition, mill operators intentionally divert pulping liquors from the process during certain maintenance operations and during process start-ups and shut downs (20).

Liquor losses and spills not only adversely affect economic operation of the pulping process but can also adversely affect wastewater treatment system operations and lead to increased effluent discharges of conventional and toxic pollutants. These wastewater treatment systems operate most effectively when influent variability is minimized. Thus, achievement of minimum effluent discharges is only possible at mills where routine liquor losses, intentional liquor diversions, and unintentional liquor spills are effectively controlled.

These BMPs focus on controlling spent pulping liquor losses and intentional liquor diversions from chemical pulp mills to control toxic pollutants for the following reasons:

- (1) Spent pulping liquor spills and intentional liquor diversions are a principal cause of upsets and loss of efficiency in biological wastewater treatment systems that are nearly universally used for the treatment of chemical pulp mill wastewaters. The resulting interference with biological treatment system operations can lead to pass-through of conventional pollutants, priority pollutants, and non-conventional pollutants that would otherwise be treated or removed.
- (2) Losses of pulping liquor are a significant contribution to untreated wastewater loadings and discharge loadings of color, oxygen-demanding substances, and non-chlorinated toxic compounds from chemical pulp mills.
- (3) Prevention and control of spent pulping liquor losses is a form of pollution prevention that will result in less demand for pulping liquor make-up chemicals; increased energy efficiency through recovery of liquor solids; more effective and less costly wastewater treatment system operations; and reduced formation of wastewater treatment sludges.

- (4) Control of spent pulping liquor losses will result in incidental reductions in atmospheric emissions of Total Reduced Sulfur (TRS) compounds from kraft mills and volatile hazardous air pollutants (HAPs) from all chemical pulp mills implementing these BMPs.

This document presents information on BMPs for controlling losses of spent pulping liquor, soap and turpentine. Section 2.0 summarizes EPA's legal authority to promulgate BMP requirements. Wood composition is described in Section 3.0. The major chemical pulping and recovery processes are briefly reviewed in Section 4.0. The chemical composition and toxicity of pulping liquors, soap and turpentine are described in Section 5.0. Sources of pulping liquor losses are described in Section 6.0. Current industry practices regarding spent pulping liquor management, spill prevention, and control are reviewed in Section 7.0, along with discussion of spill containment measures for soap and turpentine. The BMP requirements are described in Section 8.0. Estimated costs, effluent reduction benefits, and current industry status with respect to implementing BMPs are presented in Section 9.0.

2.0

LEGAL AUTHORITY

In the BMP regulation codified at 40 CFR 430.03, EPA is requiring mills with pulp production in the Bleached Papergrade Kraft and Soda Subcategory (Subpart B) and the Papergrade Sulfite Subcategory (Subpart E) to implement BMPs to prevent or otherwise contain leaks and spills and to control intentional diversions of spent pulping liquor, soap, and turpentine. These BMPs apply to direct and indirect discharging mills within these subcategories and are intended to reduce wastewater loadings of non-chlorinated toxic compounds and hazardous substances. The same BMPs will also remove, as an incidental matter, significant loadings of color and certain oxygen-demanding substances in pulping liquors that are not readily degraded by biological treatment. EPA also expects incidental reductions in conventional water pollutants and certain air pollutants as a result of the BMPs.

EPA's legal authority to promulgate this BMP regulation is found in Section 304(e), Section 307(b) and (c), Section 308(a), Section 402(a)(1)(B), Section 402(a)(2) and Section 501(a) of the Clean Water Act, 33 U.S.C. § 1251, et seq. EPA also relies on 40 C.F.R. § 122.44(k). This BMP regulation is also consistent with the Pollution Prevention Act of 1990, 42 U.S.C. § 13101, et seq.

For authority to impose BMPs on direct discharges, EPA relies in part on section 304(e) of the Clean Water Act. EPA is authorized under section 304(e) to publish regulations on a categorical basis for certain toxic or hazardous pollutants for the purpose of controlling plant site runoff, spillage or leaks, sludge or waste disposal, and drainage from raw material storage, when the Administrator determines (1) that such incidents are associated with or ancillary to the industrial manufacturing or treatment process of point sources within the class or category, and (2) that the incidents may contribute significant amounts of toxic or hazardous pollutants to navigable waters. The BMPs in today's regulations are directed, among other things, at preventing or otherwise controlling leaks, spills and intentional diversions of phenol, acetic acid, benzoic acid, carbon disulfide, p-cresol, formaldehyde, formic acid, hydrogen sulfide, methyl mercaptan, and sodium hydroxide from spent pulping liquor at mills with pulp production in Subparts B and E. See Chapter 5. EPA has designated phenol as a toxic pollutant under CWA section 307(a)(1),

see 40 C.F.R. § 401.15, and has designated acetic acid, benzoic acid, carbon disulfide, p-cresol, formaldehyde, formic acid, hydrogen sulfide, methyl mercaptan, and sodium hydroxide as hazardous substances under CWA section 311, see 40 C.F.R. § 116.4. Turpentine, in turn, is ignitable, which is a characteristic of section 311 hazardous substances under 40 CFR Part 302. Turpentine and the wastes from which it is derived (foul condensates) also contain two listed section 311 hazardous substances--hydrogen sulfide and methyl mercaptan--and the priority pollutants phenol and toluene. Soap has a very high BOD₅ content and contains materials that exhibit significant toxicity to fish (see Section 5.6 for further discussion).

The Administrator has determined that leaks, spills and intentional diversions of spent pulping liquor containing these pollutants are associated with various chemical pulping processes discussed in Chapter 6, *infra*. The Administrator has also determined, for the reasons set forth in Chapter 5, that failure to prevent or control the leaks, spills and intentional diversions of spent pulping liquor could cause significant amounts of phenol and the identified hazardous substances to enter the Nation's waters. In addition to phenol and the § 311 hazardous pollutants identified above, EPA has also identified a number of other toxic compounds in spent pulping liquors from bleached papergrade kraft and sulfite mills that can have significant adverse effects on navigable waters. These toxic pollutants are identified in Table 5-9, *infra*. Chapter 5, *infra*, also discusses the effects of spent pulping liquor and soap on the toxicity of mill effluent. EPA intends that the BMPs established in this regulation will control the toxic effects of these pollutants. As the U.S. Court of Appeals for the D.C.Circuit observed after reviewing the goals of the Clean Water Act and its legislative history, "The indications are abundant that EPA was intended to possess broad latitude in identifying and regulating suspected toxics." NRDC v. EPA, 822 F.2d 104, 118 (D.C. Cir. 1987)(upholding EPA regulation requiring information in permit applications regarding effluent characteristics); see Statement of Sen. Muskie (Dec. 15, 1977), 95th Cong., 2d Sess., reprinted in A Legislative History of the Clean Water Act of 1977, Vol. 3, at 453-54 (1978) (citing a spill of mirex to illustrate need for § 304(e) authority, even though mirex is not designated as a § 307(a) toxic pollutant or a § 311 hazardous substance).

For authority to impose BMPs on direct discharges, EPA also relies on sections 402(a) and 501(a) of the Clean Water Act and 40 C.F.R. § 122.44(k) of EPA's regulations. Under section 402(a)(1), the Administrator is authorized to issue a permit "upon condition that [the] discharge will meet either all applicable requirements under sections 301, 302, 306, 307, 308, and 403 of this Act, or prior to the taking of necessary implementing actions relating to all such requirements, such conditions as the Administrator determines are necessary to carry out the provisions of this Act." EPA's authority to establish permit conditions under this section is very broad. See NRDC v. Costle, 568 F.2d 1369, 1380 (D.C. Cir. 1977). As applied in this context, section 402(a)(1) authorizes EPA to establish controls on "any pollutant, or combination of pollutants," for which EPA has not yet promulgated effluent limitations guidelines or standards under sections 301 or 306 that would be applicable to the permittee in question. With the exception of pH, total suspended solids (TSS) and biochemical oxygen demand (BOD), EPA has not promulgated effluent limitations guidelines or standards applicable to Subparts B and E for the pollutants associated with spent pulping liquor, soap, or turpentine. See Tables 5-1 through 5-9. While EPA expects that the BMPs will result in incidental removals of TSS and BOD, the BMPs are intended to prevent or control the releases of the other pollutants identified in the tables cited. In addition, section 402(a)(2), read in concert with section 501(a), authorizes EPA to prescribe as wide a range of permit conditions as the Agency deems appropriate in order to assure compliance with applicable effluent limits. (Section 501(a) authorizes the Administrator to carry out her functions through regulation.) EPA has determined that mills without an adequate BMP program, such as that codified in the BMP regulation, may experience undetected and uncontrolled leaks and spills that could disrupt the efficiency of their treatment systems, thus resulting in exceedances of the BAT limitations and NSPS promulgated for Subparts B and E. See, e.g., Chapter 1.

Moreover, EPA's regulations at 40 C.F.R. § 122.44(k) specifically require permit writers to impose, when applicable, BMP permit conditions to control or abate the discharge of pollutants in any case when "[n]umeric effluent limitations are infeasible" or when "[t]he practices are reasonably necessary to achieve effluent limitations and standards or to carry out the purposes and intent of [the] CWA." 40 C.F.R. § 122.44(k)(2) & (3). EPA has determined that it is

infeasible to establish numeric effluent limitations for each pollutant likely to be controlled by BMPs because leaks and spills in particular tend to be accidental, unpredictable releases and EPA is unable to specify with any degree of certainty the quantities of pollutants to be regulated. See NRDC v. Costle, 568 F.2d at 1380. Moreover, numerical effluent limitations are best suited for operational discharges deemed to represent application of best available (or demonstrated) technologies or implementation of numeric water quality criteria; they are not as effective or efficient as BMPs to prevent leaks and spills. Finally, the stated goal of the Clean Water Act is to eliminate the discharge of pollutants into the Nation's waters. CWA section 101(a)(1). EPA has determined that BMPs, by preventing or controlling leaks, spills or intentional diversions, are an important step toward that goal, particularly with respect to toxic and other pollutants. See CWA section 101(a)(1) & (3). Therefore, EPA has determined that BMPs applicable to all pollutants in a mill's spent pulping liquor, soap, and turpentine were necessary in order to carry out the purposes of the Clean Water Act and hence are authorized under section 402(a)(1) and 40 CFR 122.44(k).

Although a requirement to establish and implement BMP plans of the type described in this regulation could be imposed on a case-by-case basis under authority of section 402(a)(1) and 40 C.F.R. § 122.44(k), EPA has decided to promulgate the requirement on a categorical basis for the class of facilities subject to Subparts B and E of Part 430 under section 304(e) and under its broad authority conferred by section 501(a). Section 304(e) expressly authorizes EPA to promulgate BMPs by regulation on a categorical basis. The spent pulping liquors, soap, and turpentine covered by these BMPs contain numerous toxic pollutants and hazardous substances subject to section 304(e), and hence may be controlled by regulation. In addition, section 501(a) authorizes the Administrator to prescribe such regulations as are necessary to carry out her functions under the Act. EPA has determined that the BMP program of the type specified in § 403.03 is necessary to ensure that each pulp and paper mill with pulp production in Subparts B or E prevent or otherwise contain leaks and spills, and that they control intentional diversions, of spent pulping liquors, soap and turpentine. While the BMP regulation is intended to provide considerable flexibility to mills in designing their BMP programs, EPA has also determined that the various BMPs specified in the regulation represent the minimum elements of any effective

BMP program. By codifying them into a regulation of general applicability, EPA intends to promote expeditious implementation of a minimum BMP program and to assure uniform and fair application of the baseline requirements. EPA also believes that the regulation represents an appropriate and efficient use of its technical expertise and resources that, when exercised at the national level, will relieve state permit writers of the burden of implementing this aspect of the Clean Water Act on a case-by-case basis. Thus, in order to ensure that minimal BMPs are in place for mills in Subparts B and E and to promote efficient administration of the NPDES permit program, EPA is promulgating BMPs for Subparts B and E by regulation.

EPA also relies on Section 308(a) as authority to require mills to develop and implement a BMP Plan as prescribed in § 430.03, and to perform attendant monitoring and reporting functions. Section 308(a) authorizes EPA, among other things, to require owners or operators of point sources to establish and maintain records, make reports, install, use and maintain monitoring equipment, sample effluent, and provide such other information as the Administrator may require in order to carry out the objectives of the Act. Among other things, EPA expects that the permitting authority will be able to use the information to monitor the mills' compliance with the regulation's BMP implementation requirements. See Sections 308(a)(2) and 402(a)(2). In addition, EPA expects that information provided by mills under § 430.03 will assist EPA to evaluate the effectiveness of the BMP program it has designed.

An important aspect of the BMP program codified by EPA is the flexibility it provides to mills in deciding how to implement the various specified measures. This is consistent with the legislative history for Section 304(e), which EPA regards in this rulemaking as sensible direction for the BMPs, even when imposed under other CWA authorities. Statement of Rep. Roberts (Dec. 15, 1977), 95th Cong., 2d Sess., reprinted in A Legislative History of the Clean Water Act of 1977, Vol. 3, at 341 (1978). It is also consistent with EPA's practice of not prescribing specific technologies to achieve the performance objectives. By granting mills considerable flexibility to choose the most cost-effective strategies for preventing and otherwise controlling leaks, spills and intentional diversions of spent pulping liquors, soap, and turpentine, EPA intends to maximize the opportunity for the individual point source to consider various factors, e.g., the

facility's age, type of pulp processes, the physical configuration of the mill, and mill-specific constraints associated with recovery boilers and evaporator and treatment systems, when implementing the BMP program.

For authority to impose BMPs on indirect discharges, EPA relies on Sections 307(b) and (c) of the Clean Water Act. Pretreatment standards for new and existing sources under Section 307 are designed to prevent the discharge of pollutants that pass through POTWs or that interfere with or are otherwise incompatible with treatment processes or sludge disposal methods at POTWs. To determine whether pollutants associated with spent pulping liquors, soap, and turpentine that are indirectly discharged by mills in Subparts B and E interfere with POTW operations or pass through untreated, EPA reviewed data collected from 1988 through 1992 at a POTW that receives effluent from a bleached papergrade kraft mill. See Chapter 9.3.1. Prior to 1990-91, the mill had virtually no facilities for control and collection of spent pulping liquor leaks and spills. POTW discharge monitoring records show the fully treated effluent exhibited consistent chronic toxicity to *Daphnia* from April 1988 until June 1991. The data further show that the toxic effects of the POTW's effluent have been reduced since implementation by the mill of effective spent pulping liquor management and spill prevention control. See Chapters 5.4 and 9.3.1 and Tables 9-1, 9-2 and 9-3. These effluent toxicity effects can be related to the wood extractive components that are measurable by COD and are found in leaks and spills of spent kraft and sulfite pulping liquors that interfere with the performance of biological treatment systems and allow toxic pollutants to pass through inadequately treated. Indeed, evidence of such interference and pass through was found in data from this mill and the POTW, which showed higher mass effluent loadings for COD, TSS, and BOD before the mill implemented a BMP program. After the BMP program was implemented, mass effluent loadings of these pollutants were reduced. Data for COD, in particular, indicated that short-term interference of POTW operations previously observed at higher COD levels was being mitigated. See Chapter 9.3.1. These data led EPA to conclude that leaks and spills of spent pulping liquor interfered with POTW operations. Data from the mill also show the effect of inadequate turpentine control on POTW operations and caused pass through of pollutants. See Chapter 9.3.1. Soap can also exhibit toxic effects on aquatic life and biological treatment systems. See Chapter 5.6. EPA also considered a

case study of an incident in 1993 where a diversion of pulping liquor debilitated the mill's secondary treatment system and killed fish in the receiving water. See Chapter 8 for a more detailed discussion of this incident. Because direct discharging mills using these BMPs achieve very high removals and because POTWs cannot achieve similar removals in the absence of BMPs employed by the indirect discharger, EPA has determined that pollutants in spent pulping liquor, soap and turpentine, in the absence of controls on leaks, spills and intentional diversions, can cause disruption and interference and do pass through POTWs. For this reason, EPA is including as part of its pretreatment standards the requirement that mills implement BMPs in accordance with this regulation. EPA was unable to establish numeric PSES for the pollutants of concern because the interference occurred only sporadically in response to infrequent and unpredictable leaks and spills. However, EPA concluded that the BMP Program codified in section 430.03 will minimize the interference and pass through attributable to those pollutants and perhaps prevent it altogether.

3.0 WOOD COMPOSITION

The principal components of wood are cellulose, hemicelluloses, lignin, and extractives.

Cellulose is a linear polysaccharide consisting of *B-D*-glucopyranose units linked by (1-4)-glucosidic bonds. Cellulose molecules are bundled together in wood to form microfibrils, which in turn build up to form fibrils, and finally cellulose fibers. About 40% of most wood is cellulose that has a molecular weight of greater than 10,000. (1)

Hemicelluloses are composed of different carbohydrate units. Unlike cellulose, hemicelluloses are branched to various degrees, and their molecular masses are much lower. The content and type of hemicellulose found in softwoods differs considerably from that found in hardwoods. In softwoods, galactoglucomannans (15-20% by weight), arabinoglucuronoxylan (5-10%), and arabinogalactan (2-3%) are the most common hemicelluloses; in hardwoods, glucuronoxylan (20-30%) and glucomannan (1-5%) are the most common hemicelluloses. (1)

Lignin is essentially an aromatic polymer. It is formed in wood by an enzyme-initiated dehydrogenative polymerization of a mixture of three different 4-hydroxyarylpropenyl alcohols. The proportions of these alcohols vary with different wood species. Softwood lignin is largely a polymerization product of coniferyl alcohol. The aromatic content of softwood lignin, expressed as monomeric phenol, is about 50%. In hardwoods, lignin is formed by copolymerization of coniferyl and sinapyl alcohols. Lignin is probably chemically linked to hemicelluloses. The relative molecular mass of native lignin is considered infinite. Lignin imparts rigidity to the fiber walls and acts as a bonding agent between fibers. (1)

"Extractives" are components of the wood that can be extracted by organic solvents such as ethanol, acetone, or dichloromethane. Extractives include aliphatic extractives, which consist of fats and waxes; phenolic extractives, which consist of hydrolyzable tannins, flavonoids, lignans, stilbenes, and terpenes; and terpenoid compounds (found only in softwoods), which include mono-, sesqui-, and diterpenes; and various resin acids. The amount of extractives in wood varies greatly (1.5 to 5%), depending on the species, place of growth, and age of the tree (1). Many of the compounds classified as extractives, particularly the resin and fatty acids, which are

discharged in wastewaters from pulping operations, have been found to be toxic to aquatic life (2,3,4,5). Table 3-1 summarizes some of the extractives found in wastewaters from kraft, sulfite, and mechanical pulping operations. Although many of these compounds exhibit toxicity to aquatic life, they have not been designated specifically as "priority pollutants" under the CWA by EPA.

Table 3-1**Extractive Compounds Associated with Wood Pulping Operations**

Extractive Compound	Kraft Pulping	Sulfite Pulping	Mechanical Pulping
Resin Acids			
Abietic	•	•	•
Dehydroabietic	•	•	•
Isopimaric	•	•	•
Palustric	•	•	•
Pimaric	•	•	•
Sandaracopimaric	•	•	•
Neoabietic	•	•	•
Unsaturated Fatty Acids			
Oleic	•	•	•
Linoleic	•	•	•
Linolenic	•	•	•
Palmitoleic	•	•	•
Diterpine Alcohols			
Pimarol			•
Isopimarol			•
Abienol			•
12E-abienol			•
13-epimanool			•
Juvabiones			
Juvabione		•	•
Juvabiol		•	•
• 1'-dehydrojuvabione		•	•
• 1'-dehydrojuvabiol		•	•
Lignin Degradation Products			
Eugenol		•	
Isoeugenol		•	
3,3'-dimethoxy-4,4'-dihydroxystilbene		•	

Sources: Kringstad and Lindstrom, 1984 (1); Springer, 1986 (2); Leach and Thakore, 1974 (3).

4.0 WOOD PULPING AND CHEMICAL RECOVERY SYSTEMS

4.1 Pulping Processes

In 1992, the United States pulp and paper industry produced nearly 66 million tons of wood pulp by the following processes (6):

Process	Percent of Production	Thousands of Tons
Bleached Sulfate (Kraft)	45.0	29,703
Unbleached Sulfate	33.7	22,228
Semi-Chemical	6.2	4,101
Thermomechanical	5.4	3,584
Groundwood and Refiner	4.4	2,917
Total Sulfite	2.2	1,427
Dissolving and Special Alpha	2.1	1,383
Other	~1.0	600
Total	100.0	65,943

The distinguishing characteristics and major products associated with these pulping processes are summarized below.

4.1.1 Mechanical Pulp

4.1.1.1 Stone Groundwood Pulp

Stone groundwood pulp is produced by forcing logs against a grindstone by mechanical pressure. Nearly all of the log is converted into a low-grade pulp used primarily for newsprint and other products where permanence is not an important factor. Lignin, which binds wood fibers together, imparts color to pulp, and causes paper to yellow, is not removed in this process. Other products made from stone groundwood pulp include towels, inexpensive writing paper, and molded products such as egg cartons.

For newsprint production, groundwood pulp is usually blended with about 20% chemical pulp for added strength. Groundwood pulp is usually not bleached; if it is bleached, it is not bleached to a high degree of brightness. The frayed and broken fibers obtained from groundwood pulping are quick to absorb printing inks and thus are suitable for high-speed printing.

4.1.1.2 Refiner Mechanical Pulp

In this process, wood chips are passed through double-disc steel refiners, where the fibers are mechanically separated rather than ground on a stone. The fibers are frayed for better bonding, but they are not chopped indiscriminately as in the stone groundwood process. Consequently, refiner mechanical pulp is stronger than stone groundwood pulp and is more suitable for certain uses where strength is an important factor.

4.1.1.3 Thermomechanical Pulp

Thermomechanical pulp is produced by preheating wood chips with steam before refining (as described in Section 4.1.1.2). The heat acts to soften the lignin, which binds the wood fibers together, and promotes fiber separation. This process results in a stronger pulp than that produced by the groundwood process and minimizes the need for blending with more expensive chemical pulp in newsprint production.

4.1.2 Semi-Chemical Pulp

In this process, wood chips are processed in a relatively mild chemical solution before mechanical refining for fiber separation, usually with disc refiners. The chemical solution most often consists of a sodium sulfite/sodium carbonate liquor which acts to soften the lignin and promote fiber separation; thus, the product is often called neutral sulfite semi-chemical (NSSC) pulp. Other pulping liquors and chemical solutions may also be used to produce semi-chemical pulp. The yield of semi-chemical pulping depends on the specific process used; it ranges from 65 to 85%. Most semi-chemical pulp is not bleached and is used for corrugated board,

newsprint, and specialty boards. Bleached NSSC pulp can be used to manufacture writing and bond papers, offset papers, tissues, and towels.

4.1.3 Chemical Pulp

More than 90% of the wood pulp manufactured in the United States is produced by the kraft (sulfate) and sulfite chemical pulping processes (6). The purposes of chemical pulping are to remove lignin to facilitate fiber separation and to improve the papermaking properties of the fibers. The kraft process is the most widely used commercial process by far, accounting for more than 88% of U.S. wood pulp production in 1992 (6). Dissolving kraft and sulfite mills are operated to produce high-grade cellulose pulp for selected product applications. Soda pulping is similar to kraft pulping, except that sulfur is not intentionally added to the cooking liquor. A summary of the number of mills using various pulping processes is provided below (7):

Type of Mill	Number of Mills	Number of Mills With Bleaching
Kraft and Soda Mills		
Dissolving Grade Kraft	3	3
Papergrade Kraft	107	85
Papergrade Soda	2	2
Total	112	90
Sulfite Mills		
Dissolving Grade Sulfite	4	4
Papergrade Sulfite	11	10
Total	15	14

Kraft pulping entails treating wood chips in the range of 170• C under pressure with an alkaline pulping liquor that contains sodium hydroxide (NaOH) and sodium sulfide (Na₂S). The pulping liquor and pulping conditions promote cleavage of the various ether bonds in the lignin. The lignin degradation products dissolve in the liquor. Sodium sulfate (Na₂SO₄) and lime (CaO) are used to replenish the pulping liquor as part of the chemical and energy recovery operations associated with the process. Depending on pulping conditions, as much as 90-95% of the lignin

can be removed from wood in kraft pulping (1). The yield for kraft pulping is typically about 50%. In kraft pulping for the production of bleached pulp, more than 55% of the total weight of wood is dissolved in the pulping liquor.

Portions of the wood polysaccharides, especially those associated with the hemicelluloses, and most of the wood extractives, are dissolved in the kraft pulping liquor. If softwood is the raw material, the extractives can be recovered as by-products such as sulfate turpentine and tall oil. Turpentine contains a mixture of the lower terpenes, whereas raw tall oil (i.e., soap) consists mainly of fatty and resin acids. The content of residual extractives in unbleached (brownstock) pulp is low (1).

After separation from the pulp, the spent pulping liquor is evaporated to a high concentration and then burned in a recovery boiler to recover energy and inorganic chemicals, which are used to re-constitute fresh pulping liquor (1).

By comparison, lignin is solubilized in the sulfite process through sulfonation at elevated temperatures. The pulping liquor contains sulfur dioxide and alkaline oxides (sodium, magnesium, or calcium) (1). Ammonia is also used as a base chemical for sulfite pulping.

The lignin content of brownstock (unbleached) pulp manufactured for production of bleached pulp is characterized by two measures: (1) the Kappa Number¹, and (2) the Permanganate number or K Number. The K Number is a short test that can be performed within one hour and produces results that are about one-third lower than corresponding Kappa Numbers for softwood pulps and 30 percent lower for hardwood pulps. Kappa Numbers for conventionally pulped, kraft softwood brownstock pulps are generally in the range of 28 to 34; those for kraft brownstock hardwood pulps are in the range of 14 to 18. Kappa Numbers for unbleached sulfite pulps are lower than for kraft pulps, reflecting the lower amount of lignin present. Kappa

¹TAPPI Test Methods T236CM-85 (Kappa number) and UM251 (K number) (Reference 34).

Numbers for brownstock pulp that is not bleached may range from less than 60 to more than 100, which is a reflection of the higher yield desired for linerboard and other unbleached grades.

The distinguishing characteristics of the kraft and selected sulfite pulping processes are presented in Table 4-1 and are discussed further below.

4.2 Pulping and Chemical Recovery Systems

4.2.1 Kraft and Soda Pulping

Figures 4-1 and 4-2 provide simplified schematic diagrams of the kraft pulping and chemical recovery processes (8,9). Kraft pulping is economical because of the relatively efficient recovery of pulping chemicals and the energy from the pulping liquor. The kraft recovery system consists of the following major components:

- Collecting "weak black liquor" washed from pulp (12 to 20% liquor solids) and concentrating the liquor in multiple effect evaporators to "strong black liquor" (typically 50% liquor solids);
- Oxidizing black liquor, if required, for odor control at mills equipped with direct contact evaporation design recovery boilers;
- Further concentrating strong black liquor in concentrators to "heavy black liquor," typically greater than 65% liquor solids;
- Adding salt cake (Na_2SO_4) to make up soda losses (for mills with extensive TRS controls and sulfur recovery, most soda losses are made up with sodium hydroxide);
- Incinerating heavy black liquor in a recovery furnace, where the released energy is converted to steam and most of the inorganic chemicals are recovered in molten form as smelt. Some of the inorganic chemicals are recovered as the catch in air emission control systems on the recovery furnaces;
- Dissolving the smelt in a solution of weak wash from the causticizing circuit to form "green liquor";

- Causticizing the green liquor with lime to form "white liquor" for return to the digesters for pulping; and
- Reburning lime mud consisting of calcium carbonate (CaCO_3) in a lime kiln to form lime (CaO) for reuse in the causticizing circuit.

Cited references should be consulted for more detail regarding kraft pulping and recovery operations and the design of chemical process equipment. The processes for soda pulping and chemical recovery are essentially the same as those for kraft pulping; the main difference between these processes is that soda pulping does not involve the use of sulfur compounds to facilitate delignification. Hence, the TRS-related odor problems associated with kraft pulping do not occur. Soda pulping results in a lower yield and pulp strength than the kraft process. Soda pulping is most often used to pulp hardwoods.

4.2.2 Sulfite Pulping

Schematic diagrams for typical ammonia, calcium, sodium, and magnesium base sulfite pulping processes are presented as Figures 4-3 to 4-6, respectively (8,10). Mixtures of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-) are used to solubilize lignin. The lignin is removed from the cellulose as salts of liginosulfonic acid, and the lignin molecular structure remains largely intact. Sulfite pulping is performed over a wide range of pH. "Acid sulfite" denotes pulping with an excess of free sulfurous acid at pH 1 to 2, while "bisulfite" pulping is conducted under less acidic conditions in the range of pH 3 to 5 (8).

The primary differences among the sulfite pulping methods lie in the base chemical used for pulping and the extent of chemical recovery possible. Other than heat recovery from calcium base weak liquors, there are no feasible means for calcium recovery from calcium base liquors due to the formation of calcium sulfate. By-products or co-products (ligno-sulfates, yeasts)

can be derived from calcium base weak liquors through additional processing, but calcium is not returned to the process from those operations. In most ammonia base sulfite pulping, sulfur is recovered as SO_2 from burning the weak liquor, but ammonia is combusted and lost from the system (Figure 4-4).

The recovery systems for sodium base sulfite pulping are somewhat similar to kraft recovery systems in that the weak liquor is concentrated with evaporators and combusted in recovery boilers. A molten smelt is recovered and reconstituted, and sulfur is recovered as SO_2 and reused to prepare fresh cooking acid (Figure 4-5). Recovery of magnesium base liquors is accomplished in specially designed recovery furnaces where, unlike kraft recovery boilers, no smelt is produced. Rather, the combustion products are carried through the furnace and recovered as magnesium oxide in cyclonic separators. The separators are followed by gas/liquid contactors, where the remaining particulates and SO_2 are scrubbed with a magnesium hydroxide solution to regenerate the cooking liquor (Figure 4-6). A number of commercial sulfite liquor recovery systems are available. Figure 4-7 presents a summary of sulfite recovery systems currently in use (11).

4.2.3 Semi-Chemical Pulping

Figures 4-8 and 4-9 provide simplified schematic diagrams of a semi-chemical pulp mill utilizing continuous digestion and a fluidized bed system for treatment of NSSC waste liquor, respectively. Semi-chemical pulping liquors may range from sodium hydroxide alone (cold soda) to alkaline sulfite liquors to mixtures of sodium hydroxide and sodium carbonate to kraft green or white liquors. At semi-chemical mills co-located at kraft or sulfite pulp mills, pulping liquors are processed by cross-recovery with kraft or sulfite liquors. Where cross recovery is not feasible, the fluidized bed system illustrated in Figure 4-9, or a similar system, is usually used.

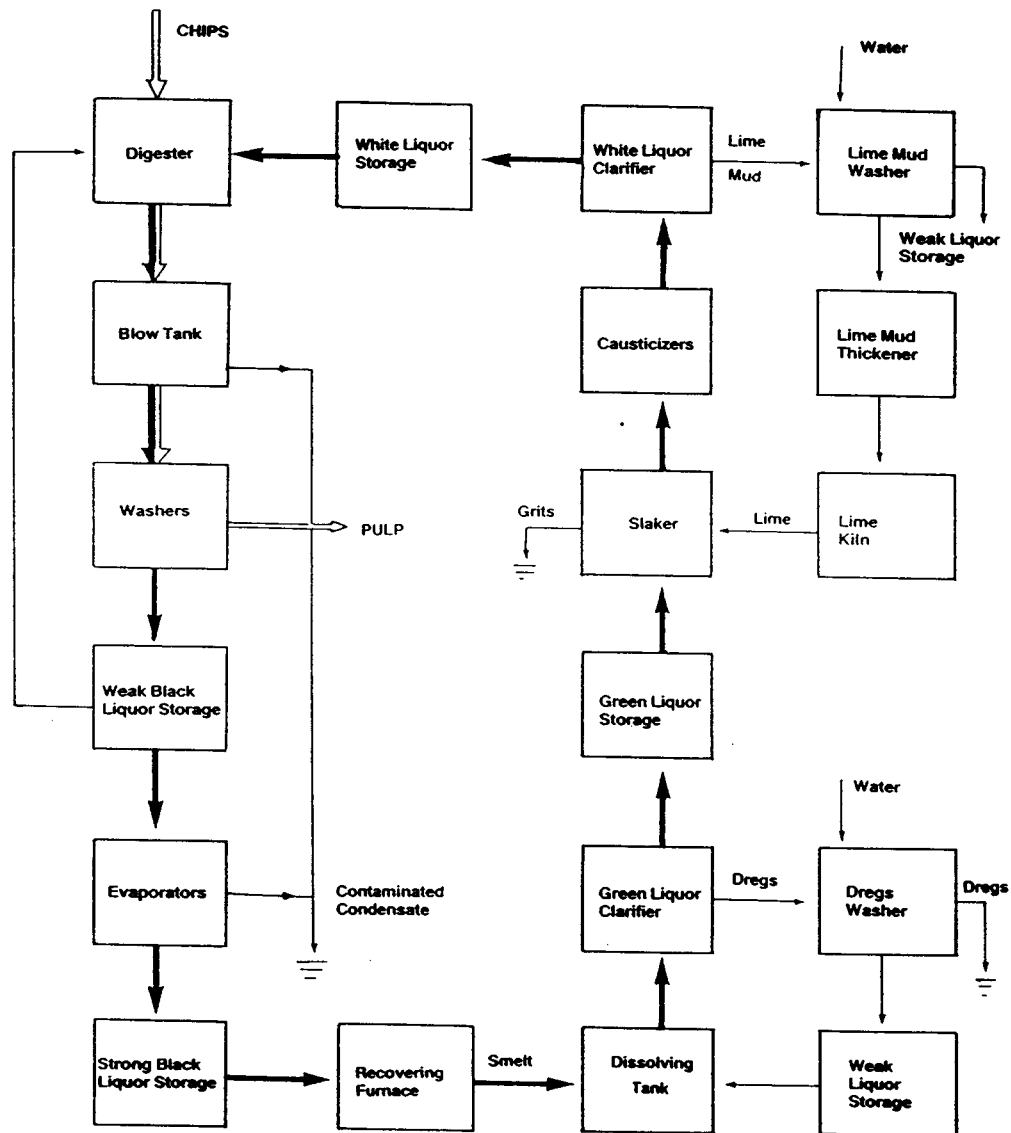
Table 4-1**Comparison of Kraft and Sulfite Pulping Processes**

Process Characteristic	Kraft Process	Sulfite Process
Cellulosic Raw Material	Almost any kind of wood, soft or hard	Any hardwood and non-resinous softwood; must be of good color and free of certain hydroxy phenolic compounds
Principal Reaction in Digester	Hydrolysis of lignins to alcohols and acids; mercaptans are formed	Sulfonation and solubilization of lignin with bisulfite; hydrolytic splitting of cellulose-lignin
Composition of Cooking Liquor	12.5 % solution NaOH, Na ₂ S, and Na ₂ CO ₃	7 % by weight SO ₂ , of which 4.5 % is present as sulfurous acid, and 2.5 % Ca, Na, NH ₃ or Mg(HSO ₃) ₂
Cooking Conditions	2 to 5 hours at 340-350 °F and 100-135 psi	6 to 12 hours at 257-320 °F and 90-110 psi
Chemical Recovery	Most of process is devoted to recovery of cooking chemicals, with energy recovery from burning organic matter dissolved in liquor. Chemical losses are replenished with salt cake, Na ₂ SO ₄ .	SO ₂ relief gas recovered; Mg or Na liquor recovered after wood digestion and washing. Ammonia can be recovered in some ammonia-base pulping systems.
Pulp Characteristics	Brown color; difficult to bleach; strong fibers; resistant to mechanical refining	Dull white color; easily bleached; fibers weaker than kraft fibers
Typical Paper Products	Strong brown bag and wrapping; multiwall bags; gumming paper; building paper; white papers from bleached kraft; paperboard for cartons, containers, and corrugated board	Book paper, bread wrap, sanitary tissue

Sources: EPA, 1982 (5); Green and Hough, 1992 (9); Ingruber, et al., 1985 (11).

Figure 4-1

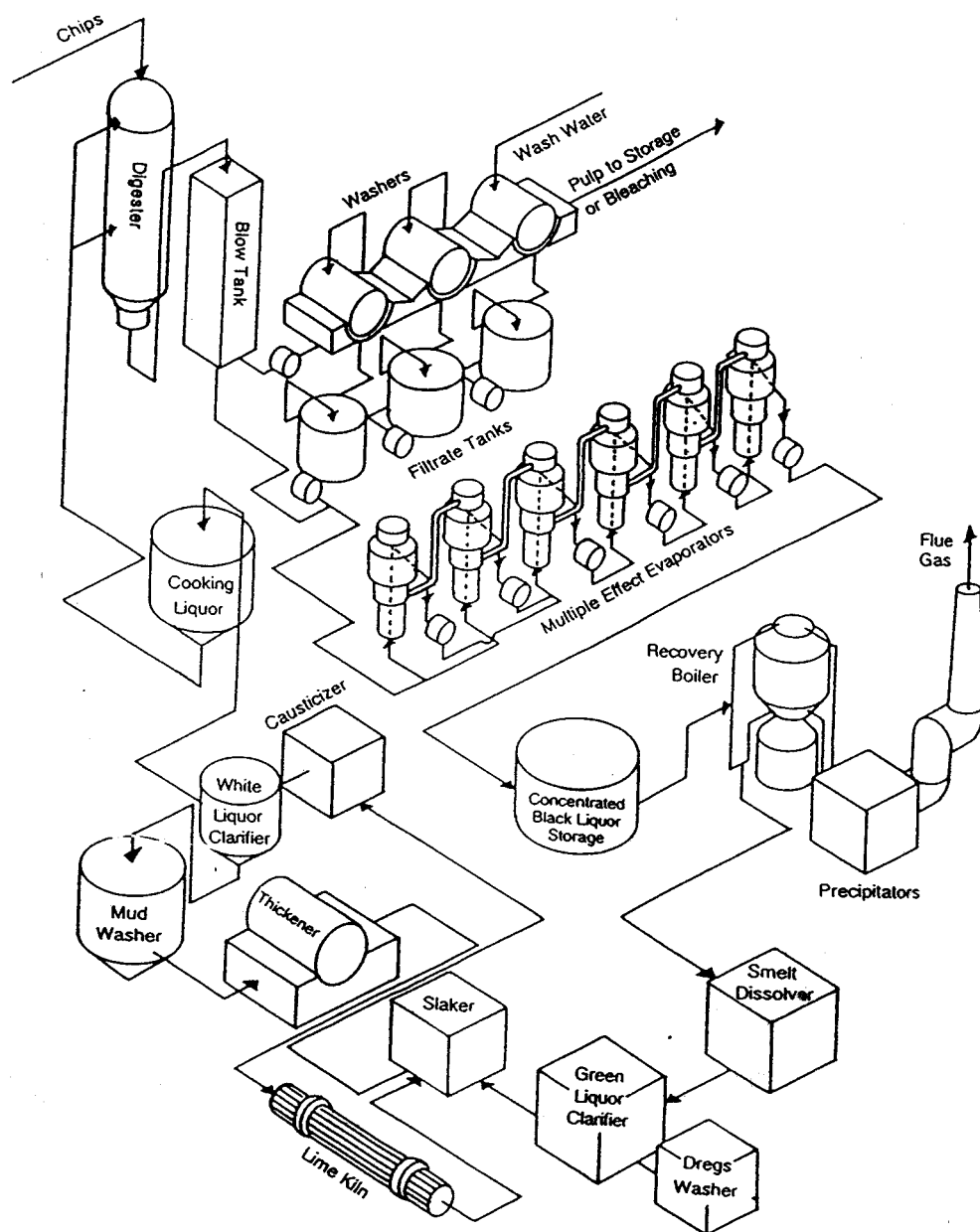
Kraft Process Simplified Schematic Diagram



Source: Smook, 1989 (8)

Figure 4-2

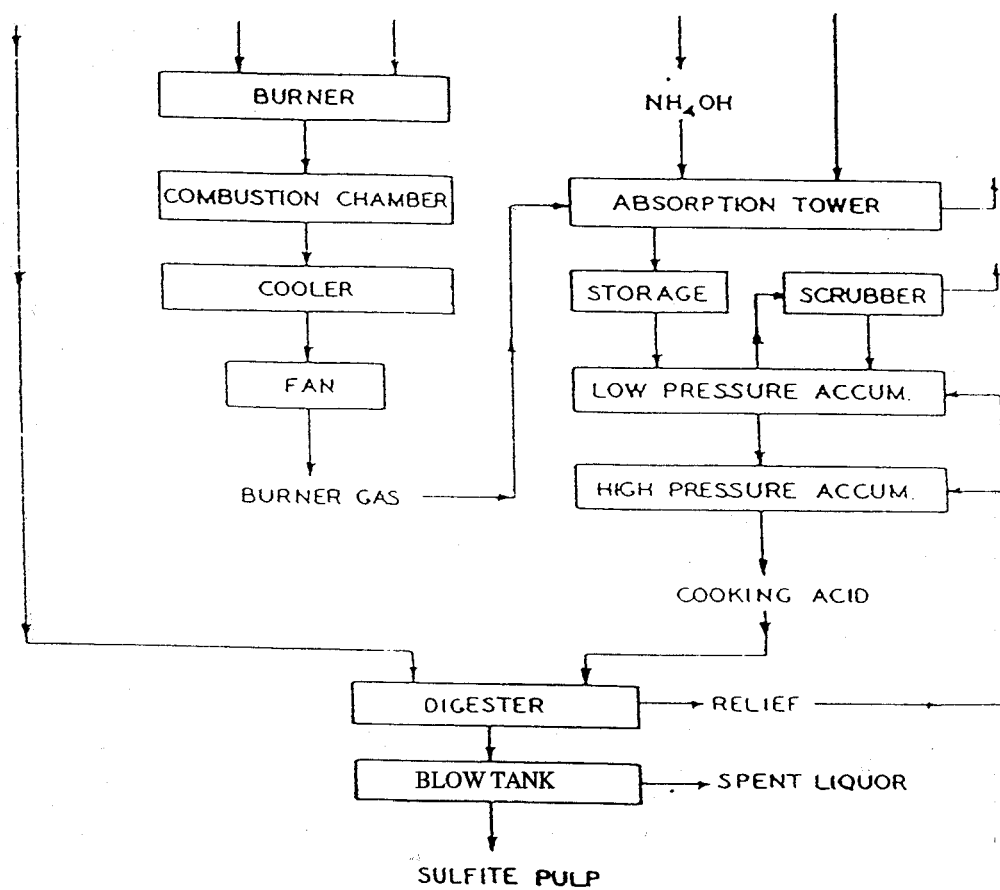
Kraft Pulping and Chemical Recovery Simplified Schematic Diagram



Source: Green and Hough, 1992 (9)

Figure 4-3

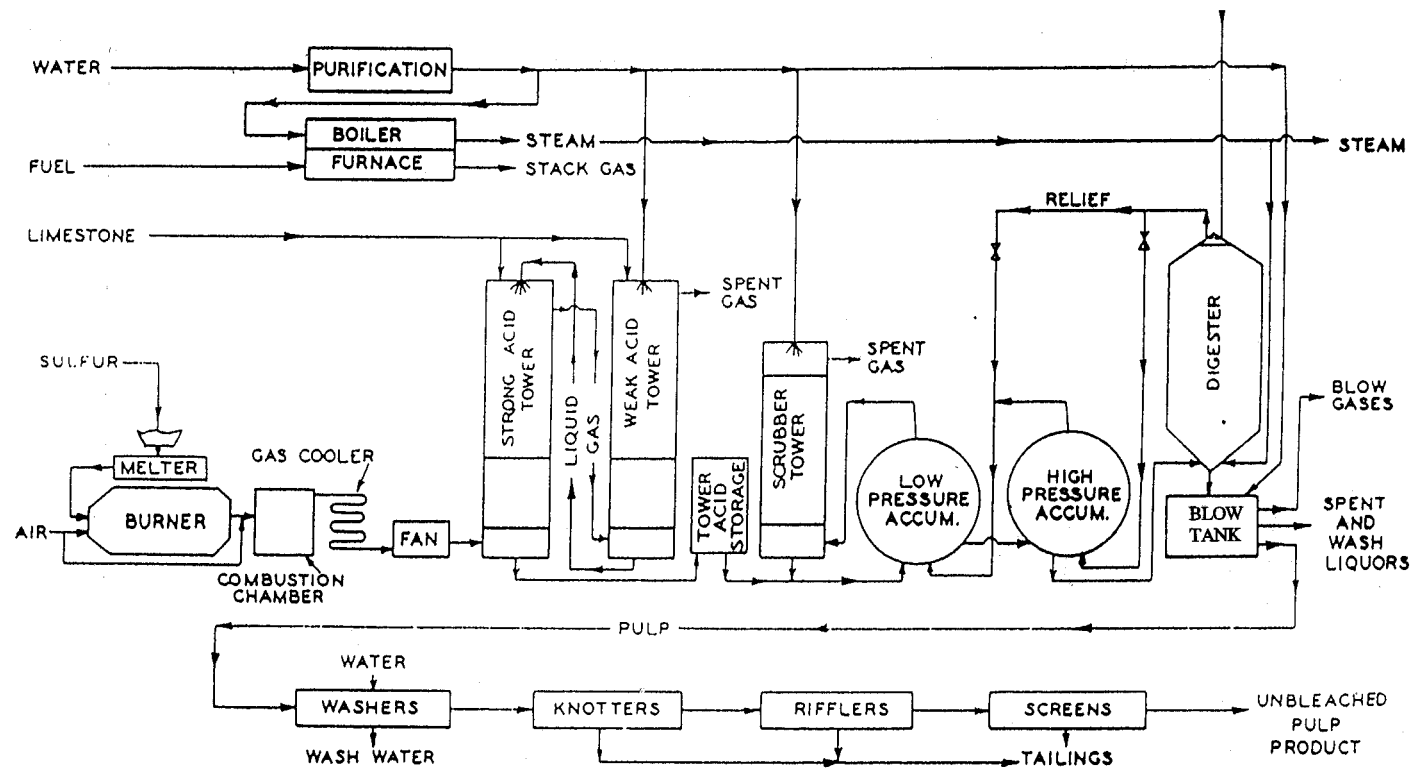
**Ammonia Base Sulfite Pulping
Simplified Schematic Diagram**



Source: Libby, 1962 (10)

Figure 4-4

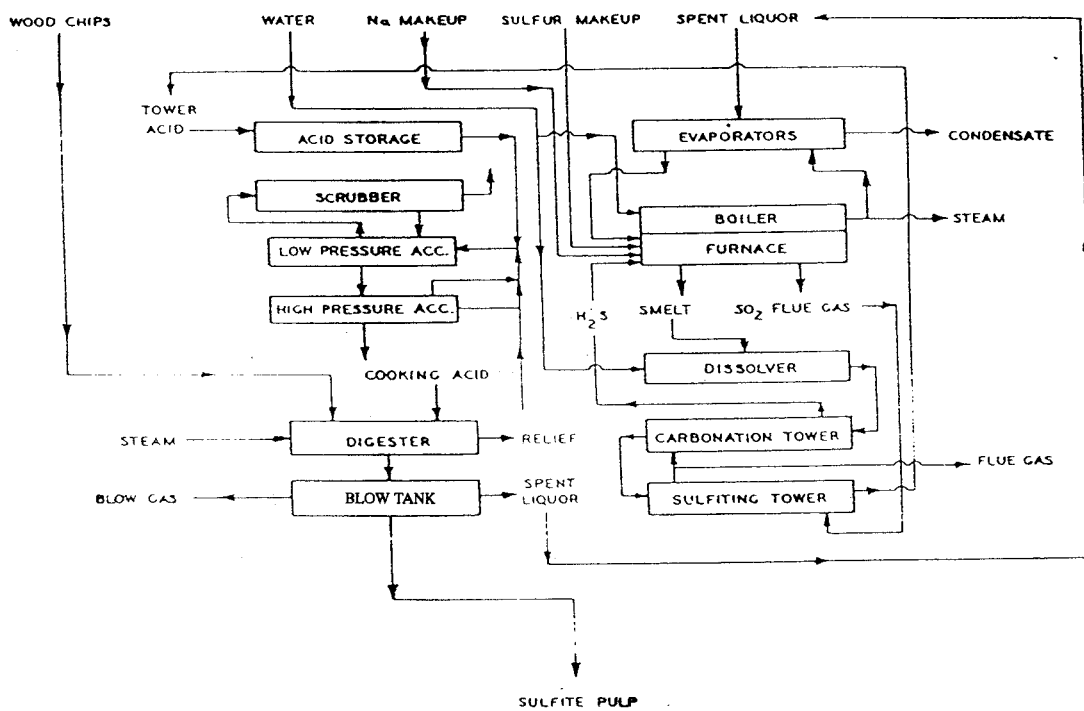
Calcium Base Sulfite Pulping Simplified Schematic Diagram



Source: Libby, 1962 (10)

Figure 4-5

Sodium Base Sulfite Pulping Simplified Schematic Diagram



Source: Libby, 1962 (10)

Figure 4-7

Sulfite Recovery Systems Currently in Use

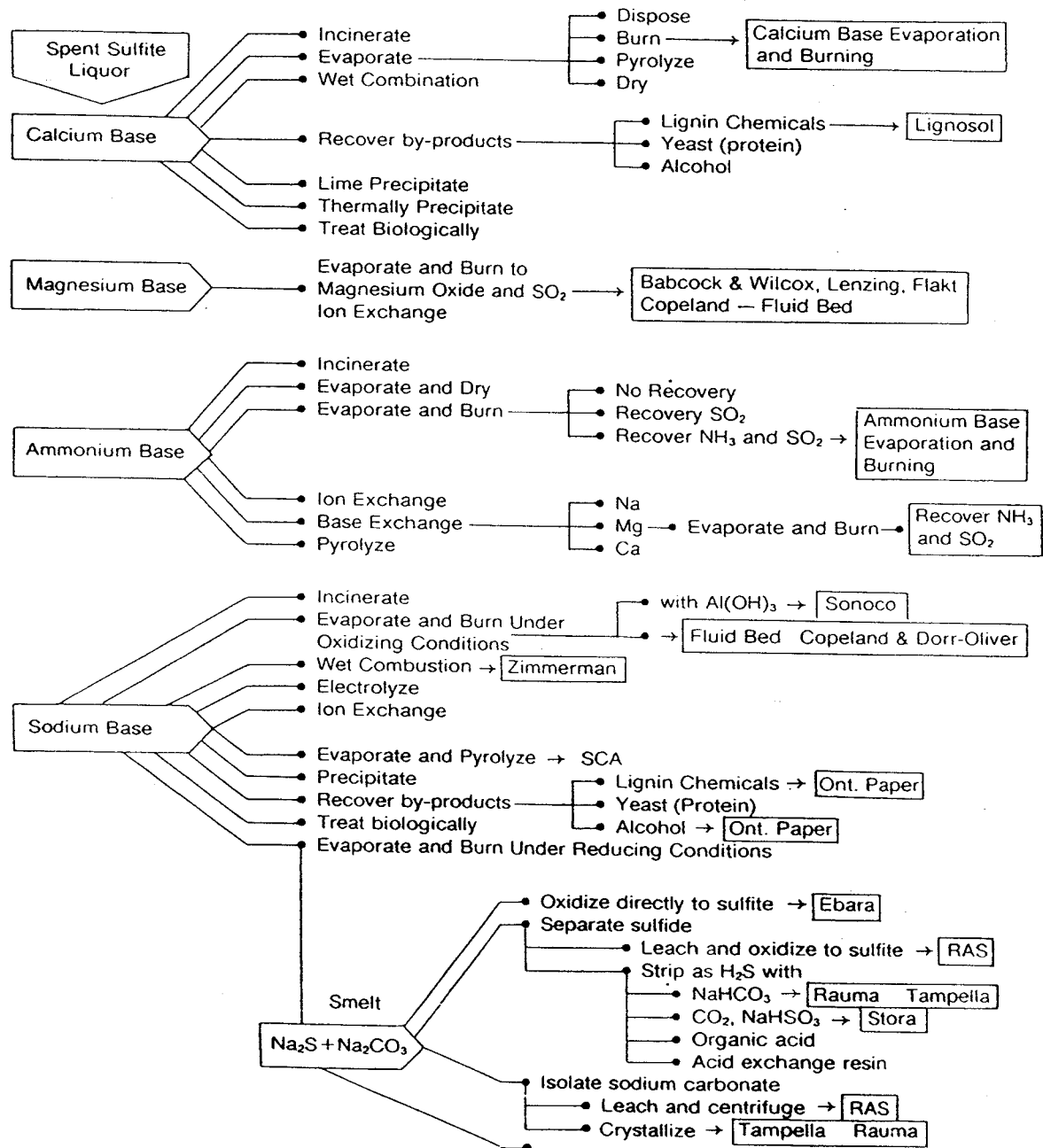
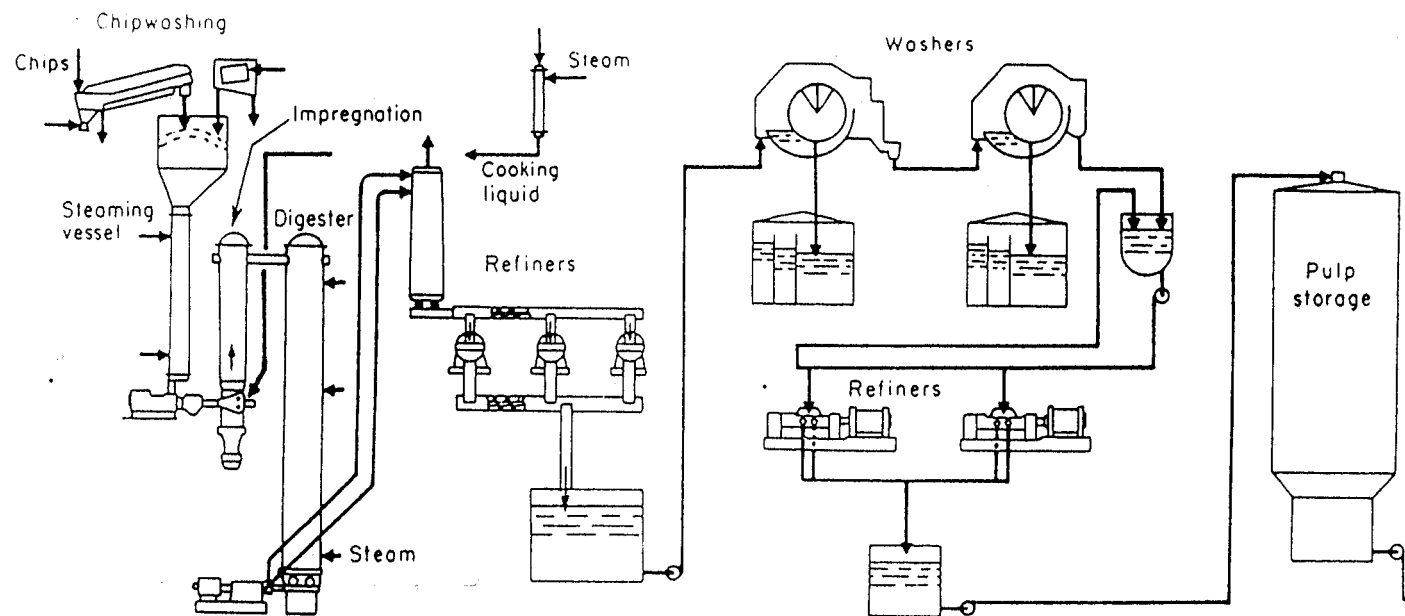


Figure 4-8

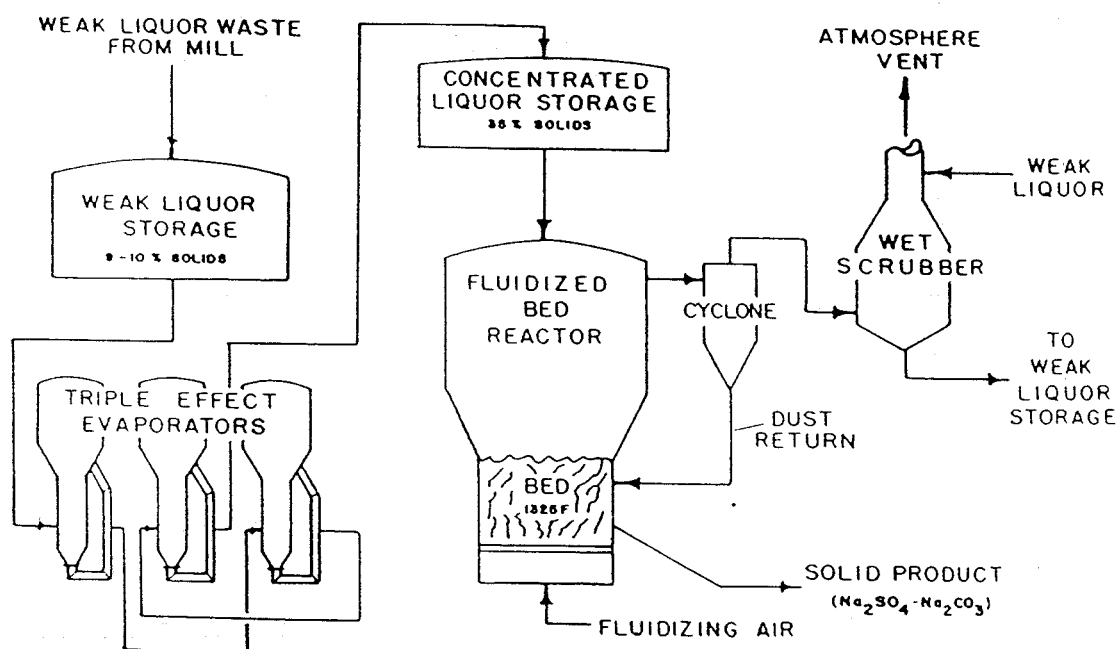
**Semi-Chemical Pulping Mill Utilizing Continuous Digestion
Simplified Schematic Diagram**



Source: Smook, 1989 (8)

Figure 4-9

**Fluidized Bed System For Treatment of NSSC Waste Liquor
Simplified Schematic Diagram**



Source: Smook, 1989 (8)

5.0 COMPOSITION AND TOXICITY OF PULPING LIQUORS, SOAP, AND TURPENTINE

5.1 Kraft Mill Black Liquor

The chemical composition of black liquor is of particular interest because of the adverse impact pulping liquors can have on biological wastewater treatment facilities, the potential for discharge of chemicals toxic to aquatic life, and the emission of TRS and HAPs to the air.

Weak black liquor recovered from brownstock pulp washing may have a liquor solids content ranging from about 12% to as high as 20%, depending on the brownstock washing systems used and the mill's operating practice. The typical elemental analysis for black liquor from a bleached kraft mill with a pulp mix of 80/20 softwood/hardwood and a higher heating value (HHV) of 6,030 British thermal units per pound (BTU/lb) of liquor solids is as follows (8):

Constituent	Percent of Black Liquor Solids
Sodium (Na)	19.2
Sulfur (S)	4.8
Carbon (C)	35.2
Hydrogen (H)	3.6
Oxygen (O)	35.2
Potassium (K)	1.0
Chloride (Cl)	0.1
Inerts	0.2

Liquors that have greater heating values (up to 6,500 BTU/lb of liquor solids) will tend to have a higher fraction of carbon, and less oxygen and sodium; the opposite is true of liquors that have lower heating values (9).

The primary inorganic constituents in black liquor include:

- Sodium Hydroxide (NaOH);
- Sodium Sulfide (Na₂S);

- Sodium Carbonate (Na_2CO_3);
- Sodium Sulfate (Na_2SO_4);
- Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$); and
- Sodium Chloride (NaCl).

These compounds originate from the white liquor used for pulping, although small amounts may also be introduced with the wood (9). Table 5-1 presents a summary of the inorganic content of black liquors measured at 27 kraft mills (9). Dissolved wood substances in black liquors consist of four types of substances: (1) ligneous materials (polyaromatic in character); (2) saccharinic acids (degraded carbohydrates); (3) low-molecular-weight organic acids; and (4) extractives (resins and fatty acids) (9). The organic constituents are combined chemically with sodium hydroxide in the form of sodium salts. Considerable differences in liquor quality from pulpwoods are reported, particularly between softwoods and hardwoods (9). Typical ranges of black liquor solids are listed below:

Constituent	Percent of Black Liquor Solids
Alkali Lignin	30-45
Hydroxy Acids	25-35
Extractives	3-5
Acetic Acid	5
Formic Acid	3
Methanol	1
Sulfur (S)	3-5
Sodium (Na)	17-20

Table 5-2 presents supplemental detailed data for black liquor components for four pine liquors and one spruce liquor (9).

5.2 Sulfite Pulping Liquors (Red Liquors)

Table 5-3 presents the compositions of one calcium base and two magnesium base sulfite pulping liquors, and Table 5-4 presents the compositions of four ammonia base and twelve sodium base

sulfite pulping liquors (11). The ammonia base liquors have higher levels of organic materials, as measured by BOD₅, COD, and dissolved organic compounds; are about an order of magnitude more toxic than calcium base and magnesium base liquors; and are about five times more toxic than sodium base liquors. The toxicity emission factors (TEFs) presented in Tables 5-3 and 5-4 are based on static 96-hour bioassays and are factored to the volume of liquor production. The presence of ammonia compounds in ammonia base liquor is the likely cause of the higher toxicity.

5.3 Semi-Chemical Pulping Liquors

The compositions of typical NSSC fresh and spent pulping liquors are presented in Tables 5-5 and 5-6, respectively (11).

5.4 Toxicity of Pulping Liquors

The toxicity of wood pulping liquors has been extensively studied for many years. The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI, formerly the National Council of the Pulp, Paper and Paperboard Industries for Stream Improvement) conducted studies with the Institute of Paper Chemistry in the 1940s and 1950s to determine the toxicity of components of kraft mill pulping wastes (12,13,14). NCASI reported minimum lethal concentrations of several compounds for certain species of *Daphnia* and *Pimephales promelas* (fathead minnows). These concentrations are summarized in Table 5-7.

The results presented in Table 5-7 show that hydrogen sulfide, methyl mercaptan, crude sulfate soap, and sodium salts of fatty and resins acids are among the components of black liquor that are toxic to *Daphnia* and freshwater minnows. Minimum lethal concentrations in the low parts per million (ppm) were found for these compounds. McKee and Wolf also summarized compilations of toxicity data for components of sulfate (kraft) liquors to fish (15). These data (some of which are included in Table 5-7) are presented in Table 5-8.

More recent studies of in-mill toxicity at a northern Ontario (Canada) bleached kraft mill resulted in the following recommendations to reduce effluent toxicity (in priority ranking) (16):

- Improve black liquor spill control system;
- Provide total countercurrent recycle of brownstock washers;
- Dedicate No. 1 Mill to hardwood production;
- Improve condensate system;
- Improve digester plant;
- Eliminate liquor carryover to blow heat condensate;
- Upgrade No. 1 Mill evaporators; and
- Improve soap recovery.

At this mill, the pulp mill sewer was found to contribute 55% of the effluent toxic loading, while the combined condensate and (bleach plant) acid sewer contributed 25% and 20%, respectively. Of the eight recommendations to reduce effluent toxicity, the two with the highest priority (and five of the eight recommendations), were directed at reducing the amount of black liquor lost from the processes. Improvements to the black liquor spill control system were cited as the measures that would have the greatest impact on reducing effluent toxicity.

Toxic impacts to the aquatic environment by compounds associated with kraft pulping liquors have also been reported. A large spill of black liquor from a kraft mill resulted in "massive fish mortalities" at the time of the spill. It was estimated that natural recolonization of the river by native fish would take several years (17). In another well documented case, a large release of spent pulping liquor and contaminated condensate resulted in failure of the wastewater treatment plant which, in turn, resulted in an NPDES permit exceedance and a moderate fish kill in the receiving river (32, 33). Also, sublethal toxic effects in rainbow trout have been attributed to the accumulation of dehydroabietic acid discharged from a kraft mill (18).

At a large southern United States bleached kraft paperboard mill, the process wastewater effluent is discharged to a local POTW; this wastewater comprises more than 95% of the combined industrial and municipal wastewater volume treated at the POTW. The POTW provides biological treatment with an aerated stabilization basin similar to those installed at many kraft

mills. A portion of the pulp produced at the mill is bleached. Prior to 1990-1991, the mill had essentially no facilities for the control and collection of black pulping liquor spills and leaks. POTW discharge monitoring records show the fully treated effluent exhibited consistent chronic toxicity to *Daphnia* from April 1988 until June 1991.

During 1989 and early 1990, when the mill was undergoing extensive upgrading, POTW operating records document over 100 incidents of black pulping liquor losses from the mill. During that time, there were numerous violations of the POTW NPDES permit effluent limitations for TSS, BOD₅, and toxicity effluent limitations. NPDES permit operating data for the period of December 1988 through December 1992 showed intermittent acute toxicity of the effluent to *Daphnia* from mid-1989 through early 1990, and consistent chronic toxicity to *Daphnia* until mid-1991, at which time installation of most of the spent pulping liquor spill prevention and control facilities was completed (19).

The mill underwent a major upgrade during much of 1989 and early 1990. A series of construction problems resulted in heavier-than-normal black liquor losses to the sewer, which hampered POTW operations. POTW performance with respect to conventional pollutant discharges improved in 1992, coinciding with implementation of effective spent pulping liquor management, spill prevention, and control at the mill (see Section 9.4).

5.5 Toxic Pollutants Found in Spent Pulping Liquors

EPA collected samples of spent pulping liquors from four kraft mills and one sulfite mill for analysis of toxic wastewater pollutants and volatile organic compounds, including HAPs. The results of these analyses are presented in Table 5-9. These data show that phenol was detected in sulfite red liquor at 882 • g/L, and in samples of hardwood and softwood kraft black liquor at concentrations ranging from 1,200 micrograms per liter (• g/L) to more than 50,000 • g/L, which exceeds the water quality criteria for phenol. See 45 Fed. Reg. 79318, 79338 (November 28, 1980) and supporting record. Based on this information, EPA has determined that spills, leaks or intentional diversions of spent pulping liquor could contribute significant amounts of phenol to

U.S. waters. One softwood black liquor sample was analyzed for zinc and found to contain 272 • g/L. This level, though significant, is below chronic and acute water quality standards (31). However, it has been EPA's longstanding view that the appearance of a chemical on the section 307(a) toxic pollutant list indicates the potentially toxic effects of its discharge. See 44 Fed. Reg. 32854, 32897 (June 7, 1979) (promulgation of general 304(e) BMP regulations).

In addition, the following compounds found in spent pulping liquors and/or turpentine (and the wastes from which it is derived) have been identified in EPA's list of hazardous substances as codified at 40 C.F.R. §116.4: acetic acid, benzoic acid, carbon disulfide, *p*-cresol, formaldehyde, formic acid, hydrogen sulfide, methyl mercaptan and sodium hydroxide. EPA has examined the levels of these substances present in spent pulping liquor and, in the case of hydrogen sulfide and methyl mercaptan, turpentine as they relate to potential releases that are preventable through implementation of BMPs. "Average" preventable daily releases, "maximum" releases (determined by adjusting the average daily release to account for variability in release volumes at a mill prior to implementation of BMPs), and a "catastrophic" spill (based on failure of a 300,000 gallon spent pulping liquor storage tank) were used as a basis for quantifying the potential avoided releases of hazardous substances listed. The analysis showed that potential releases of acetic acid and formic acid exceeded the "minimum reportable quantity limit", as defined in 40 CFR 302.4, for both the maximum release and catastrophic spill scenarios (35). Therefore, EPA has determined that spills, leaks, or intentional diversions of spent pulping liquors and turpentine could contribute significant amounts of hazardous substances to U. S. waters.

5.6 Toxic and Hazardous Pollutants Found in Turpentine and Soap

Turpentine and soap (tall oil), commonly called wood extractives, are normal components of kraft mill spent liquor resulting from cooking the wood in a mixture of alkaline chemicals under the normal manufacturing conditions. By weight, extractives comprise about 5% of wood, but in terms of total COD are about 8% because of the high carbon content of many of the compounds. Some components, such as methanol, are a result of chemical reactions that degrade other constituents of the wood, particularly lignin. However, the majority of the compounds come

from the resinous material in softwood, commonly called pitch. For practical purposes there are virtually no similar components in hardwoods.

Crude sulfate turpentine (generally known as simply "turpentine" in the kraft industry) is a complex mixture of volatile compounds obtained from the pitch component of wood. Turpentine leaves the kraft manufacturing process with the foul condensates formed when steam from the cooking and black liquor evaporation is condensed.

Turpentine is relatively easy to separate from the digester blow condensate, both batch and continuous, by decanting it and removing the top layer containing the insoluble turpentine. Crude turpentine is often sold to reprocessors who purify it for sale to end users. It is also frequently used as a fuel in the mill, effectively destroying all organic components, including the priority pollutants.

Table 5-10 shows the major components of kraft foul condensates and their location in the process. Two of the compounds listed as phenolics are phenol and toluene. Both compounds are on the list of priority pollutants. Many other compounds found in crude turpentine are extremely toxic and in addition, turpentine is ignitable.

There is no specific data available on the fraction of the contaminants in the foul condensates that remain with the separated turpentine, but in view of the relatively simple flotation type separation systems used, and the well known tendency for the separation to fail from time to time due to carry-over of black liquor, it is apparent that most of the contaminants found in the condensates were also found in the turpentine at least on occasion.

In addition to high BOD₅ content¹, soap and some of its constituents have been shown to be highly toxic to fish, with minimum lethal concentration levels similar to listed hazardous substances (see Tables 5-7 and 5-8). A 1947 NCASI technical bulletin (12) identified sulfides,

¹Reported to be as high as 850,000 to 950,000 mg/L at one mill (26).

5.0 Composition and Toxicity of Pulping Liquors

mercaptans, and soap components as the kraft pulping liquor constituents with greatest potential for harming aquatic life if released in abnormally large quantities.

Table 5-1

**Inorganic Content of Black Liquors
(Weight Percent, Dry Solids Basis)**

Constituent	Average	Minimum	Maximum
Sodium Carbonate	8.7	6.6	12.3
Sodium Sulfate	3.2	0.9	8.3
Active Alkali as Na ₂ O	6.0	3.9	8.6
Sodium	18.7	17.2	20.5
Potassium	1.4	0.4	2.7
Sulfur	3.8	2.6	6.2
Sulfated Ash	62.1	57.3	69.2

Source: Green and Hough, 1992 (9)

Table 5-2

**Components in Black Liquors
(Weight Percent, Dry Solids Basis)**

Component	Pine Liquor	Pine Liquor	Pine Liquor	Pine Liquor	Spruce Liquor
Lignin	28.9	30.7	31.1	42	41
Hemicellulose and Sugars	1.14	0.11	1.3		
Extractives	6.69	2.53	5.7		3
Saccharinic Acids			18.8		28
Acetic Acid*	3.52	2.08	5.2	3.83	5
Formic Acid*	4.48	2.7	3.1	3.37	3
Other Organic Acids	5.5	2.22			
Methanol					1
Unknown Organic Compounds	19.0	29.5	5.8	25.6	
Inorganic Salts	18.6	18.5	20.3	25.6	
Organically Combined Sodium	10.1	10.3	8.7		
Unknown Inorganic Compounds	2.08	1.35			
Sulfur					3
Sodium					16
Total	100	100	100	100	100

*§ 311 hazardous substance

Source: Green and Hough, 1992 (9)

Table 5-3

**Composition of Calcium Base and Magnesium Base
Sulfite Pulping Liquors**

Characteristic	Calcium Base	Magnesium Base		
	Mill 3	Mill 1	Mill 4B	Average
Pulp Yield (%)	46	54	45	50
Liquor Volume ⁽¹⁾ (m ³ /ODT)	9.28	6.56	5.61	6.08
pH	5.3	3.4	3.3	--
TOC (kg/ODT)	NT ⁽²⁾	NT ⁽²⁾	NT ⁽²⁾	NT ⁽²⁾
BOD (kg/ODT)	357	169	275	222
COD (kg/ODT)	1,533	807	1,144	975
Dissolved Organics (kg/ODT)	1,043	651	913	782
Dissolved Inorganics (kg/ODT)	250	173	79	126
UV Lignin (kg/ODT)	800	469	533	501
Total Sugars (kg/ODT)	264	94	165	129
Reduced Sugars (kg/ODT)	238	32	180	106
TEF ⁽³⁾	422	316	NT ⁽²⁾	--

- Notes:
- (1) Estimated liquor volume a few minutes before "blow."
 - (2) NT - Not Tested.
 - (3) TEF - Toxicity Emission Factor
(100%/96hr LC₅₀, %) × Liquor Volume (m³/ODT pulp)
(TEF approach in Table 5-3 was not developed by EPA.)

Source: Ingruber, et al., 1985 (11)

Table 5-4**Composition of Ammonia Base and Sodium Base Sulfite Pulping Liquors**

Characteristic	Ammonia Base (4 Mills)			Sodium Base (12 Mills)		
	Average	Minimum	Maximum	Average	Minimum	Maximum
Pulp Yield (%)	42.5	41	45	62	50	80
Liquor Vol ⁽¹⁾ (m ³ /ODT)	9.46	9.11	9.73	7.10	4.92	10.67
pH	--	1.5	3.3	--	2.1	4.8
TOC (kg/ODT) ⁽⁴⁾	NT ⁽²⁾	NT ⁽²⁾	NT ⁽²⁾	697	322	1,652
BOD (kg/ODT)	413	319	464	235	151	371
COD (kg/ODT)	1,728	1,553	1,872	938	476	1,757
Dissolved Organics (kg/ODT)	1,223	1,167	1,283	595	188	1,178
Dissolved Inorganics (kg/ODT)	12.5	7.0	20	226	95	348
UV Lignin (kg/ODT)	892	822	1,009	410	202	853
Total Sugars (kg/ODT)	288	210	329	137	52	278
Reduced Sugars (kg/ODT) ⁽⁴⁾	212	160	257	74	11	218
TEF ⁽³⁾	3,663	3,313	4,378	714	423	1,208

- Notes:
- (1) Estimated liquor volume a few minutes before "blow."
 - (2) NT - Not Tested.
 - (3) TEF - Toxicity Emission Factor
(100%/96hr LC₅₀ %) x Liquor Volume (m³/ODT pulp)
(TEF approach in Table 5-4 was not developed by EPA.)
 - (4) Results for TOC and Reduced Sugars for sodium base liquor are based on data for 8 mills and 11 mills, respectively. Results for all other parameters are based on data for 12 mills.

Source: Ingruber, et al., 1985 (11)

Table 5-5**Composition of Typical Fresh NSSC Pulping Liquors**

Chemical Compound	Concentration (grams/liter as chemical)
Sodium Sulfite	133
Sodium Hydroxide *	5.8
Sodium Sulfate	3.2
Sodium Thiosulfate	< 0.1
Sodium Sulfide	< 0.1
Total Sodium	53.0
Total Sulfur	35.1

*§ 311 hazardous substance

Source: Ingruber, et al., 1985 (11)

Table 5-6**Composition of Typical Spent NSSC Pulping Liquors**

Characteristic	Average	Minimum	Maximum
pH	--	6.5	8.5
Total Solids (%)	12	8	22
Volatile Solids (%) (percent of Total Solids)	47.9	43	52
BOD ₅ (mg/l)	25,000	16,000	50,000
Acetate (mg/l)	18,000	12,000	20,000
Wood Sugars (mg/l) (mostly pentoses)	7,000	5,000	10,000
Lignin (mg/l)	45,000	25,000	85,000
Oxygen Consumption (mg/l)			
From KMnO ₄	65,000	55,000	142,000
From Ag-catalyzed dichromate	100,000	83,000	235,000

Source: NCASI, Technical Bulletin 83

Table 5-7

**Minimum Lethal Concentrations to Daphnia and Fathead Minnows of
Components of Kraft Pulp Mill Wastewaters**

Compound	Minimum Lethal Concentration (parts per million)	
	Daphnia	Fathead Minnows
Sodium Hydroxide *	100	100
Sodium Sulfide	10	3.0
Sodium Sulfate	5,000	1,000
Methyl Mercaptan *	1.0	0.5
Sodium Sulfite	300	--
Hydrogen Sulfide *	1.0	1.0
Sodium Carbonate	300	250
Sodium Sulfate	5000	100
Crude Sulfate Soap	5.0 - 10.0	5.0
Sodium Salts of Fatty Acid Fraction of Sulfate Soap	1.0	5.0
Sodium Salts of Resin Acid Fraction of Sulfate Soap	3.0	1.0

*§ 311 hazardous substance

Source: NCASI, 1947 (12)

Table 5-8

Critical Concentrations (Minimum Lethal Doses) to Fish of Components of Sulfate (Kraft) Liquors

Component	Critical Concentration (milligrams per liter)
Sodium Hydroxide *	100.0
Sodium Sulfide	3
Methyl Mercaptan *	0.5
Hydrogen Sulfide *	1.0
Formaldehyde *	50
Crude Sulfate Soap	5.0
Unsaponified Fraction of Sulfate Soap	6.0
Sodium Salts of Saponifiable Fraction of Sulfate Soap	3.0
Sodium Salts of Fatty Acids	5.0
Sodium Salts of Resin Acids	1.0
Sodium Oleates	5.0
Sodium Linoleate	10.0
Sodium Salts of Abietic Acid	3.0
Phytosterol	3.0
Sodium Thiosulfate	5.0
Sodium Sulfate	100
Sodium Chloride	2500
Sodium Hydrogen Sulfide *	0.5
Sodium Sulfide (as Sulfide)	1.2

*§ 311 hazardous substance

Source: McKee and Wolf, 1963 (15)

Table 5-9

**Toxic Wastewater Pollutants and Hazardous Air Pollutants Found in Spent Pulp
Liquors**

Analyte	Regulatory Status	Black Liquor Samples					Red Liquor Sample
		Mill 3	Mill 5	Mill 5	Mill 6A	Mill 6B	Mill 7
		SW	HW	SW	SW	SW	SW
		• g/L	• g/L	• g/L	• g/L ^a	• g/L	• g/L
Acetone	--	ND(500)	9,190	3,880	2,500	NA	2,320
Benzoic acid	HS	5,780	4,660	14,000	ND(50)	3,480	9,000
Benzyl alcohol	--	1,370	ND(100)	885	ND(10)	ND(100)	ND(53)
Benzanthrone	--	ND(500)	ND(500)	ND(500)	75.1	ND(500)	ND(263)
Bis(2-ethylhexyl) phthalate	HAP, PP	ND(100)	ND(100)	ND(100)	ND(10)	351	ND(53)
Butyl benzyl phthalate	PP	ND(100)	ND(100)	ND(100)	ND(10)	370	ND(53)
Carbon disulfide	HAP,HS	ND(100)	149	892	19.0	NA	ND(10)
p-Cresol	HAP,HS	ND(100)	ND(100)	ND(1000)	ND(10)	ND(100)	99.9
p-Cymene	HAP	1,140	ND(100)	ND(100)	ND(10)	180	418
p-Dioxane	HAP	ND(100)	890	ND(100)	ND(10)	NA	ND(10)
Hexanoic acid	--	ND(100)	ND(100)	ND(1000)	ND(10)	ND(100)	1,630
Methanol	HAP	377,000	NA	NA	535,000	366,000 ^b	<395,000 ^b
Methyl ethyl ketone	HAP	4,030	2,410	1,250	442	<1,290 ^b	ND(50)
Phenol	HAP, PP, HS	1,990	1,230	15,000	523	6,060	882
Alpha-Terpineol	--	4,930	322	827	ND(10)	14,700	64.6
1,3,5-Trithiane	--	73,300	ND(500)	193,000	ND(50)	74,400	ND(263)
Beryllium	PP	ND (0.06) ^c	NA	NA	NA	7.80	NA
Lead	PP	ND (5.4) ^c	NA	NA	NA	B 2.40	NA
Manganese	--	76.4 ^c	NA	NA	NA	2,290	NA

Table 5-9 (Continued)

Analyte	Regulatory Status	Black Liquor Samples					Red Liquor Sample
		Mill 3	Mill 5	Mill 5	Mill 6A	Mill 6B	Mill 7
		SW	HW	SW	SW	SW	SW
		• g/L	• g/L	• g/L	• g/L ^a	• g/L	• g/L
Sodium	HS	139,000 ^c	NA	NA	NA	13,300,000	NA
Zinc	PP	14.9 ^c	NA	NA	NA	272	NA

HW - Hardwood.

SW - Softwood.

HAP - Hazardous air pollutant.

PP - §307a Priority pollutant.

HS - §311 Hazardous substance.

ND - Not detected (at reported detection limit).

NA - Not analyzed.

^aConverted from units of • g/kg to • g/L.

^bAn average of several grab samples is shown.

^cUnits are mg/kg (sample contained 6.6% solids).

Table 5-10

Major Components Found in Kraft Condensate Prior to Separation of Turpentine

	Batch Digester Vent Condensate	Batch Digester Blow Condensate	Continuous Digester Flash- Steam Condensate	Evaporator Combined Condensate	Evaporator Condenser Condensate	Stripper Feed
Hydrogen sulfide, ppm	30-270	1-230	210	1-90	1-240	5-660
Methyl mercaptan, ppm	20-5,300	40-340	70	1-30	1-410	5-720
Dimethyl sulfide, ppm	15-7,400	40-190		1-15	1-15	10-1,000
Dimethyl disulfide, ppm	5-4,100	2-210		1-50	1-50	10-150
Methanol, ppm	1,800-12,000	250-9,100	570-8,900	180-700	180-1,200	140-10,000
Ethanol, ppm	90-3,200	20-900		1-190	1-130	20-1,100
Acetone	8-420	5-95		1-15	1-16	15-500
MEK, ppm	27			1-3	2	20-25
Terpenes, ppm	0.1-5,500	720-9,200	1,950-8,800	60-1,100	450-2,500	800-13,000
Phenolics, ppm	12				3	1-82
Guaiacol, ppm				1-10		
Resin acids, ppm				25-230		

Source: Blackwell et al (36).